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MEASUREMENTS OF INORGANIC IONS AND THEIR PRECURSOR GASES IN AMBIENT AIR IN FINLAND

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Title
Measurements of inorganic ions and their precursor gases in ambient air

Abstract

The objective of this thesis was to study the variability of inorganic gases and the chemical composition of particulate matter in ambient air, and to study the comparability of results obtained using novel online techniques and older measurements.

In recent decades, emissions of sulphur dioxide have decreased all over Europe and, consequently, ambient concentrations have decreased in Finland. A declining trend was also found in the concentrations of reduced nitrogen during the past years. It was found that, in addition to concentrations in air masses coming from central Europe, the transport pathways of air masses are important factors affecting concentrations in Finland. Decreasing concentrations place greater demands on measurement techniques. To ensure the comparability of the SO_2 data obtained earlier, we compared older methods to newer measurement methods.

We identified the inorganic main elements, trace elements and polycyclic hydrocarbons in PM_1, $PM_{2.5}$ and PM_{10} samples collected at the background station in Virolahti, Finland. About 70–80% of the toxic trace elements (lead, cadmium, arsenic and nickel) as well as polycyclic hydrocarbons were found in submicron particles. In practice, all the PAHs found in PM_{10} were actually present in the $PM_{2.5}$ fraction. Analysing the $PM_{2.5}$ or even the PM_1 fraction instead of PM_{10} would prove more beneficial for PAHs and trace elements, because excluding the large particles reduces the effects of the matrix during analysis. During wildfire episodes, the concentrations of the smallest particles (PM_1, $PM_{2.5}$) in particular rose. On the fire days, the potassium concentration rose in all particle fractions, but ammonium and nitrate rose only in PM_1.

One of the objectives of this thesis was to determine whether the online ion chromatograph with a one-hour time resolution could replace the filter sampling method. We successfully measured the concentrations of gases (HCl, HNO_3, HONO, NH_3, SO_2) and the major inorganic ions in particles (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) with a MARGA 2S online ion chromatograph in two size ranges in both urban and background environments. We used these short-time resolution measurements to study diurnal cycles of nitrogen-containing gases. In Hyytiälä, we found clear diurnal cycles for all the nitrogen-containing gases, especially in summer, when there is enough sunlight for photochemical reactions and possibly additional emission sources from the boreal forest environment. In winter, however, we found no diurnal cycles in either Hyytiälä or Helsinki, but in spring, diurnal cycles for HONO, HNO_3 and NH_3 resumed. In Helsinki, the results of the particles were used to study sources using trajectory analysis showing that, although continental aerosols were mostly neutralized, marine aerosols from the Norwegian Sea were not.

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Nimeke
Epäorgaanisten ionien ja kaasujen mittaukset ulkoilmasta

Tiivistelmä

Tämän väitöskirjan tavoitteena oli tutkia epäorgaanisia kaasuja ja hiukkasten kemiallista koostumusta ulkoilmassa sekä verrata uudenlaista jatkuvatoimista ionikromatografia aikaisemmin ilmanlaadun tutkimuksessa käytettyihin menetelmiin.

Viime vuosikymmenten kuluessa Euroopan rikkidioksidin emissiot ovat vähentyneet huomattavasti ja sen seurauksena pitoisuudet ovat laskeneet Suomessa. Trendianalyysin perusteella myös pelkistyneen typen pitoisuudet ovat vähentyneet. Havaittiin että Suomeen Keski-Euroopasta tulevien ilmamassojen pitoisuuksien lisäksi ilmamassojen tulosuuntien vaihtelut vaikuttavat Suomen vuosittaisiin keskiarvopitoisuuksiin ja siten trendeihin. Alentuneet ilmapitoisuudet lisäävät vaatimuksia mittausmenetelmien herkkyydelle. Aiemmin käytettyjä keräys- ja analysointimenetelmiä verrattiin uudempiin määritysmenetelmiin, jotta varmistuttiin pitkien aikasarjojen vertailukelpoisuudesta.

Virolahden tausta-asemalla määritettiin eri kokoluokkien hiukkasten (PM_1, $PM_{2.5}$ ja PM_{10}) pääionien, hivenalkuaineiden ja polysyklisten aromaattisten hiilivetyjen pitoisuudet (PAH). Tässä tutkimuksessa n. 70-80% toksisista alkuaineista (lyijy, kadmium, arseeni, nikkeli) sekä PAH-yhdisteistä oli pienimmässä alle 1 µm hiukkasfraktiossa. Käytännössä PM_{10}-hiukkasissa oleva pitoisuus oli sama kuin alle 2.5 µm hiukkasissa. Raskasmetallien ja PAH-yhdisteiden analysointi olisi kannattavampaa $PM_{2.5}$-hiukkasista, koska se vähentäisi matriisin vaikutusta. Maastopalojen aikana erityisesti pienten hiukkasten (PM_1, $PM_{2.5}$) pitoisuudet kohosivat. Samaan aikaan kaliumin pitoisuudet kohosivat sekä pienissä että karkeissa hiukkasissa. Ammonium- ja nitraattipitoisuudet kohosivat vain pienimmissä alle 1 µm hiukkasissa.

Tutkimuksessa selvitettiin myös, soveltuuko jatkuvatoiminen laitteisto korvaamaan suodatinkeräysmenetelmien käytön ilmanäytteiden määrityksissä. Jatkuvatoimisella MARGA 2S-ionikromatografilla määritettiin kaasujen (HCl, HNO_3, HONO, NH_3, SO_2) ja epäorgaanisten ionien (Cl^-,NO_3^- , SO_4^{2-} , NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) pitoisuuksia alle 2.5 µm ja alle 10 µm hiukkasissa kaupunkiympäristössä sekä Hyytiälän tausta-asemalla. Lyhyellä aikaresoluutiolla saaduista tuloksista voitiin määrittää typpihapon, typpihapokkeen ja ammoniakin vuorokausisyklit. Talvella vuorokausisyliä ei esiintynyt, mutta keväällä sekä kaupunki- että taustailman mittauksissa havaittiin vuorokausivaihtelua. Hyytiälässä kesäaikaan havaitut syklit olivat voimakkaimpia johtuen valokemiallisista reaktiosta ja mahdollisesti metsäympäristön emissioista. Helsingissä mitattujen hiukkasten kemiallista koostumusta ja trajektorianalyysia käyttäen havaittiin, että Keski-Euroopasta tulleet hiukkaset olivat yleensä neutraloituneita, mutta Norjan mereltä saapuneet hiukkaset olivat happamia.

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Helsinki, August 2014

Ulla Makkonen

ABBREVIATIONS AND DEFINITIONS

AMS	Aerosol mass spectrometer
CFC	Chlorofluorocarbons
D_p	Particle diameter (μm, nm)
DMPS	Differential Mobility Particle Sizer
EC	Elemental carbon
EMEP	European Monitoring and Evaluation Programme by the United Nations Economic Commission for Europe
FMI	Finnish Meteorological Institute
FP	Filter pack
HDPE	High-density polyethylene
HONO	Nitrous acid, HNO_2
HNO_3	Nitric acid
IC	Ion chromatograph/chromatography
ICP-MS	Inductively coupled plasma mass spectrometer/spectrometry
IVL	Svenska Miljöinstitutet, Swedish Environmental Research Institute
MARGA	Monitor for AeRosols and Gases in ambient Air), online IC
NOx	Sum of NO (nitrous oxide) and NO_2 (nitrogen dioxide)
OA-CRDS	Off-axis cavity ring-down spectrometer
OC	Organic carbon
PAH	Polycyclic aromatic hydrocarbon
PE	Polyethylene
PM_1	Particles with a diameter smaller than 1 μm (D_p < 1 μm)

PM_{10}	Particles with a diameter smaller than 10 μm ($D_p < 10$ μm)
$PM_{2.5}$	Particles with a diameter smaller than 2.5 μm ($D_p < 2.5$ μm)
PTFE	Polytetrafluoroethylene (Teflon)
SJAC	Steam jet aerosol collector
SMEAR	Station for Measuring Forest Ecosystem-Atmosphere Relations
SO_2	Sulphur dioxide
WRD	Wet rotating denuder

Contents

LIST OF ORIGINAL PUBLICATIONS

I. **Makkonen U.** and Juntto S. (1997). Field comparison of measurement methods for sulphur dioxide and aerosol sulphate, *Atmos. Environ.* **31**:7, 983-990.

II. **Makkonen U.,** Hellén H., Anttila P. and Ferm M. (2010). Size distribution and chemical composition of airborne particles in south-eastern Finland during different seasons and wildfire episodes in 2006, *Sci. Tot. Environ.* **408**, 644-651. doi: 10.1016/j.scitotenv.2009.10.050.

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1 INTRODUCTION

In the 1970s a main environmental concern was acidic deposition resulting from increased anthropogenic emissions of sulphur dioxide (SO_2) and nitrogen oxides (NO_x), as well as the long-range transport of these acidifying compounds. Several international programmes, such as EMEP (European Monitoring and Evaluation Programme by the United Nations Economic Commission for Europe), WMO BaPMoN (World Meteorological Organisation Background Air Pollution Monitoring Network), GAW (Global Atmospheric Watch) and AMAP (Arctic Monitoring and Assessement Programme), were established to monitor the environment. The acidification problem, and later also the concern about the eutrophication of natural ecosystems, underscored the importance of measurement programmes to detect changes in environmental conditions. Political decisions supported concerns about acidification, and the first European sulphur protocol (UNECE, 1985) required reductions of sulphur dioxide emissions to 30% of 1980 emissions levels by 1993, and the protocol of nitrogen oxide emissions (UNECE, 1988) attempted to limit nitrogen emissions in 1994 to 1987 levels. Thereafter, sulphur emissions successfully declined in Europe. However, the reductions of other acidic gases have proved less effective, and concern about N-containing gases persists.

Later, the emphasis on the environment shifted strongly towards global warming and climate change, as well as the effects of greenhouse gases and particles. The most abundant greenhouse gases in the atmosphere are water vapour, carbon dioxide, methane, nitrous oxide, ozone and chlorofluorocarbons (CFCs), which absorb and re-emit outgoing energy radiated from the Earth's surface, leading to the retention of heat in the lower atmosphere. In 1906–2005, the average warming trend was 0.74°C per 100 years (uncertainty range 0.56–0.92°C) (IPCC, 2013). Atmospheric particles strongly influence the climate by absorbing and scattering solar radiation, and via cloud formation and changing cloud properties. The effects of particles depend heavily on their chemical composition. For example, sulphate-containing particles scatter light, thereby cooling the climate, whereas particles containing black carbon absorb sunlight, thus contributing to global warming. Despite extensive studies on atmospheric particles, the Intergovernmental Panel on Climate Change (IPCC, 2013) still states that the radiative forcing caused by particles remains the dominant uncertainty in total radiative forcing.

In addition to effects on the climate, particles influence air quality and reduce visibility. Reduced air quality adversely affects health, especially for elderly cardio-respiratory patients, asthmatics and

children. Smaller particles are more deleterious, because they can penetrate deeper into the lungs and reach the alveoli (Malilay, 1999). In addition to particle size, effects on heath also depend on the origin and chemical composition of particles. For instance, genotoxic and carcinogenic polycyclic aromatic hydrocarbons (PAH) and trace elements are commonly found in particles originating from combustion sources (Morawska and Zhang, 2002, Vestenius *et al*., 2011 and Hedberg *et al*., 2002). To control air quality and health effects caused by particulate matter, the European Union has set limit values for PM_{10} (Directive 2008/50/EC) and member states are required to measure Pb, As, Cd, Ni and PAH in ambient particles (Directive 2004/107/EC). In addition, the Council on Ambient Air Quality and Cleaner Air for Europe (Directive 2008/50/EC) has set exposure reduction targets for $PM_{2.5}$ (particles smaller than 2.5 μm) and requires member states to measure the chemical composition of $PM_{2.5}$.

In Finland, the Finnish Meteorological Institute is responsible for performing ambient air measurements for international monitoring networks. This study has also used some of the data collected for routine monitoring measurements. This thesis focuses on the development and measurement of inorganic compounds in particulate matter and their precursor gases in ambient air for purposes of air-quality monitoring and air-chemistry studies. Most of the studies were performed at remote Nordic locations, where long-range transport is the dominant source of air pollutants. Different measurement methods for acidic gases were tested to confirm the comparability of data obtained earlier. Furthermore, gases were measured in different environments to study their seasonal and diurnal variation. In addition, the chemical composition of particles (PM_{10} and $PM_{2.5}$) was measured during different seasons and forest-fire episodes to develop the methods, to enhance our understanding of the size distribution of different compounds and to obtain measurements with more accurate time resolution.

2 OBJECTIVES OF THE STUDY

The purpose of this thesis was to study the inorganic composition of the atmosphere, as well as to test and evaluate different sampling and analysis methods for use in monitoring ambient air, especially in remote environments. The more specific objectives of this thesis were:

- to study the comparability of previous methods for monitoring SO_2 at Finnish network stations to ensure the usability of long data series and to test the suitability of diffusion denuders for SO_2 to replace the old absorption solution method (**Paper I**)
- to study the size distribution and chemical composition of particles in $PM_{1.0}$, $PM_{2.5}$ and PM_{10} during different seasons and during a wildfire episode (**Paper II**)
- to study the performance characteristics of an in-situ instrument for measuring inorganic aerosols and gases, as well as to test whether it could be used at low-concentration background sites to replace the filter method (**Papers III** and **V**)
- to obtain short time resolution data to configure diurnal and seasonal cycles of inorganic gases and aerosols at urban and rural sites (**Papers III** and **V**).
- to study the trends of reduced nitrogen compounds (**Paper IV**)

3 BACKGROUND

Acidic gases (HNO_3, HONO, SO_2) as well as ammonia (NH_3), the major base in the atmosphere, are of scientific interest with regard to acidification and air-quality effects (Seinfeld and Pandis, 2012; Galloway, 1995). In addition, these gases contribute to atmospheric nucleation and cloud formation (Ball *et al.*, 1999; Bettersheim, 2002; Kulmala *et al.*, 1998; 2000; 2013). Sulphuric acid is an important component in atmospheric nucleation, which is known to be enhanced by the presence of ammonia (e.g., Coffman and Hegg, 1995; Zhang, 2010). In addition, ions play an important role in nucleation by enhancing the nucleation process, and researchers have confirmed that ions also induce nucleation (Lovejoy *et al.*, 2004). To study particle formation and atmospheric processes, it is essential to know also the concentrations of precursor gases affecting the chemical composition of the particles formed.

The section below will first present the sources and some important reactions of HNO_3, HONO, SO_2 and NH_3, as well as those of aerosols, followed by links between gas-phase reactions and aerosol chemical composition.

3.1 Formation and reactions of inorganic gases in air

3.1.1 Sulphur dioxide

In addition to natural sources such as volcanoes (D'Alessandro *et al.,* 2013), the combustion of sulphur-containing fossil fuels in, for example, heating plants, oil refineries, industry, ships (Corbett *et al*., 1999; Stern, 2005) and wood burning (Lamarque *et al.,* 2010) emits sulphur dioxide, which, together with oxides of nitrogen, is the main compound contributing to acid deposition. Since the signing in 1985 of the first protocol for reducing sulphur emissions (the Helsinki protocol on the Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30%), concentrations of SO_2 in the air in Europe have distinctly decreased (Vestreng *et al*., 2007). In Finland in 1985, annual means varied between 2.6 and 4.9 μg S m^{-3} (the concentration of sulphur in SO_2), whereas in 1993, they were between 0.6 and 1.8 μg S m^{-3}. In 2013, annual means were even lower (i.e., between 0.1 and 0.4 μg S m^{-3}).

In the gas phase, the OH (hydroxyl) radical oxidizes SO_2 (Egsgaard *et al*., 1988). The resultant adduct reacts rapidly with O_2 to form SO_3 which in turn reacts rapidly with water to form sulphuric acid:

$$SO_2 + OH\cdot \rightarrow HOSO_2 \quad (1)$$

$$HOSO_2 + O_2 \rightarrow SO_3 + \cdot HO_2 \quad (2)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (3)$$

The HO_2 radical formed in Reaction 2 reacts further by oxidizing NO to produce an OH radical. In daytime, the OH radical is the most significant oxidant of SO_2, but at night, when the concentrations of OH radicals are lower, Criegee biradicals (from reactions of alkenes and O_3) contribute to the oxidation of SO_2 (Hatakeyama and Akimoto, 1994). The lifetime of SO_2 with respect to OH radicals in the gas phase is quite long (about 13 days), so reactions in the aqueous phase dominate. In aqueous droplets, SO_2 readily dissolves to form bisulphite and sulphite ions (Finlayson-Pitts and Pitts, 2000).

In the aqueous phase, H_2O_2 is the major contributor to the rapid oxidation of S(IV) (Gunz and Hoffmann, 1990). In addition, in the aqueous solutions with a pH close to neutral, O_2 slowly oxidizes S(IV). The reaction is more rapid, however, in the presence of Fe^{3+} and Mn^{2+} (Finlayson-Pitts and Pitts, 2000). At higher pH values, such as in sea salt particles, SO_2 is also oxidized by ozone (Keene *et al.,* 1998).

Sulphuric acid formed from the oxidation of SO_2 has very low vapour r essure $1.3 \cdot 10^{-3}$ Pa, at 23°) and therefore exists mainly condensed in water (Ayers *at al*., 1980). A sulphuric acid solution partly neutralized with NH_3 has even lower vapour pressure, which enhances particle formation (Marti *et al*., 1997).

3.1.2 Nitrous acid

Due to its rapid photolysis, HONO is an important OH source (Winer and Biermann, 1994):

$$HONO + h\nu \rightarrow OH\cdot + NO \quad \lambda < 370 \text{ nm}) \quad (4)$$

During the day, HONO can form from the reaction of an OH radical with NO but, upon exposure to sunlight, will readily photo-dissociated. HONO also forms in heterogeneous reactions of NO_2 and water on surfaces such as soot particles (Kleffmann *et al*., 1998):

$2NO_2 + H_2O \rightarrow HNO_3 + HONO$ (5)

Anthropogenic sources of HONO also exist in different combustion systems, such as cars, gas ovens and kerosene heaters, as do natural sources, such as land-cover or vegetation (Su *et al*., 2011).

HONO undergoes both a gas-phase and a heterogeneous reaction with HCl (Wingen *et al.*, 2000; Fenter and Rossi, 1996):

$HONO + HCl \rightarrow ClNO + H_2O$ (6)

Nitrous acid/nitrite can be oxidized in the aqueous phase by dissolved O_2, especially in cold conditions (Takenaka *et al*., 1996).

3.1.3 Nitric acid

Most of the HNO_3 formed in the troposphere will likely occur in heterogeneous reactions (Dentener and Cruzen, 1993):

N_2O_5 (g) + H_2O g/l) $\rightarrow 2HNO_3$ (g/aq) (7)

NO_3 (aq) + H_2O l) $\rightarrow HNO_3$ (aq) + OH (aq) (8)

Nitric acid also forms in the daytime reaction of NO_2 with the OH radical, a reaction that competes with the photo-dissociation reaction of NO_2, and at night in the reaction of NO_3 with hydrocarbons (Finlayson-Pitts and Pitts, 2000):

$NO_2 + OH \cdot \rightarrow HNO_3$ (9)

$NO_3 + RH \rightarrow HNO_3 + R$ (10)

Nitric acid has a high vapour pressure ($6.4 \cdot 10^{-3}$ Pa, at 20°) and remains in gas phase in tropospheric conditions. However, HNO_3 easily attaches to surfaces and is removed from the atmosphere rapidly through wet and dry deposition. HNO_3 reacts readily with ammonia to form an equilibrium state with ammonium nitrate (Mozurkewich, 1993):

HNO_3 (g) + NH_3 (g) $\leftrightarrow$ NH_4NO_3 (s, aq) (11)

HNO_3 reacts with the NaCl of sea salt to form $NaNO_3$:

HNO_3 (g) + NaCl s) $\rightarrow$ HCl (g) + $NaNO_3$ (s) (12)

Researchers have suggested that HNO_3 also reacts with mineral particles and particles from biomass burning to form, for example, $Ca(NO_3)_2$ (Tabazadeh *et al*., 1998).

3.1.4 Ammonia

Agricultural activities, including animal husbandry and the use of NH_3-based fertilizers, are the main sources of atmospheric ammonia, accounting for about 94% of all emissions in Europe (EEA, 2011). In addition, industries, humans, pets, wild animals, landfills and households products (Sutton *et al.*, 2000), as well as vehicles equipped with catalytic converters (Moeckli *et al.*, 1996; *Fraser et al.*, 1998) constitute other sources. In addition to anthropogenic sources such as industrial processes and vehicular emissions are also the natural emissions of NH_3 from soils (Bouwman *et al.,* 1997) and oceans (Lee *et al.,* 1998; Sørensen, 2003).

Ammonia, the most abundant base in the atmosphere, plays a major role in neutralizing acids by forming nitrates such as NH_4NO_3 (Eq. 11), NH_4HSO_4 and $(NH_4)_2SO_4$, as well as in the formation of new particles (Kirkby *et al.*, 2011; Kulmala *et al.,* 2000). In the atmosphere, ammonia can also react slowly with the hydroxyl radical, to form the amidogen radical (NH_2), which in turn reacts with nitrogen dioxide (NO_2) to form nitrous oxide (N_2O) (Park and Lin, 1997), one of the main greenhouse gases in the atmosphere (Butterbach-Bahl *et al.,* 2011).

3.2 Atmospheric particles

Atmospheric aerosols are solid or liquid particles suspended in air. Particle size, which affects the transport and deposition of the particle, is its most important characteristic. The most important impacts of particles, such as respiratory health hazards, the reduction of visibility and climate effects, depend on particle size. Particles are usually classified according to their size into the main classes: ultrafine particles (particle diameter (D_p) < 0.1 μm), fine particles (D_p < 1 μm or D_p < 2.5 μm) and coarse particles (D_p > 1 μm or D_p > 2.5 μm), as well as other classes discussed below. The limits of these classes in the literature are somewhat ambiguous. In addition, atmospheric particles can be divided according to their mechanism of formation: (i) particles emitted into the air directly from sources are primary particles, whereas (ii) particles formed from gases in the air are referred to as secondary particles (Seinfeld and Pandis, 2012).

The smallest atmospheric particles, in terms of both particle size and mass concentration, form the nucleation mode (D_p < 20 nm). Nucleation mode particles typically result form from photochemical reactions of atmospheric precursor gases, but may also be emitted by combustion sources. Sulphur is believed to play the dominant role in the formation and growth of nucleation particles (e.g., Kulmala *et al.*, 1998; 2000). The lifetime of nucleation-mode particles is rather short because the particles tend to coagulate with other particles or grow by condensation. They may also diffuse on surfaces or act as nucleation sites for droplets (Seinfeld and Pandis, 2012).

The Aitken mode particles (D_p range ~20–100 nm) form from nucleation-mode particles by condensation of various inorganic and organic gases onto nucleation-mode particles. The condensing gases may be either natural, such as organics emitted by forests (e.g., Claeys *et al*., 2004) or sulphur-containing com ounds emitted by algae in the oceans O'Dowd and de Leeuw, 2007), or anthropogenic. Combustion processes, such as wildfires, traffic, and energy production often emit primary particles in this size range (e.g., Frey *et al*., 2014). The combustion of fossil fuel produces gases containing oxidized nitrogen and sulphur compounds in addition to organics. These compounds react further in complex atmospheric oxidation processes, leading to particles containing ammonium sulphate and nitrate (Kulkarni *et al.,* 2011).

Most of the fine-particle mass is in the accumulation mode (D_p range: 0.1–1 μm), which consists of particles originating from both natural and anthropogenic sources. The mode forms through condensation of inorganic and organic gases onto Aitken-mode particles, through cloud processing of Aitken-mode particles (Hoppel *et al*., 1994), and through direct emission of primary particles, such as sea salt a rticles O'Dowd and de Leeuw, 2007), and particles emitted by combustion in energy production (e.g., Frey *et al*., 2014) and wildfires (e.g., Virkkula *et al*., 2014). The name of the accumulation mode reflects the processes: removal by diffusion, coagulation, precipitation scavenging, and sedimentation is weakest in this size range, so particles accumulate in it (Hinds, 1999; Seinfeld and Pandis, 2012). Due to the weak removal processes, accumulation-mode particles may remain in the atmosphere for weeks and be transported even thousands of kilometres; in remote areas, long-range transport is one of the main sources of particles (Laakso *et al.,* 2003). Finally, accumulation mode particles are also removed from the atmosphere through wet and dry deposition (Seinfeld and Pandis, 2012).

Coarse particles (D_p > 1 μm) typically consist of mineral particles from soil, road dust generated by vehicles, biological particles such as pollen, and coarse sea-salt particles (Kulkarni, 2011). Coarse particles are removed from the atmosphere through sedimentation and below-cloud scavenging by

precipitation (Radke *et al.*, 1980). Figure 1 presents a summary of typical mass and number size distributions of atmospheric particles, as well as chemical compositions in the different particulate size ranges.

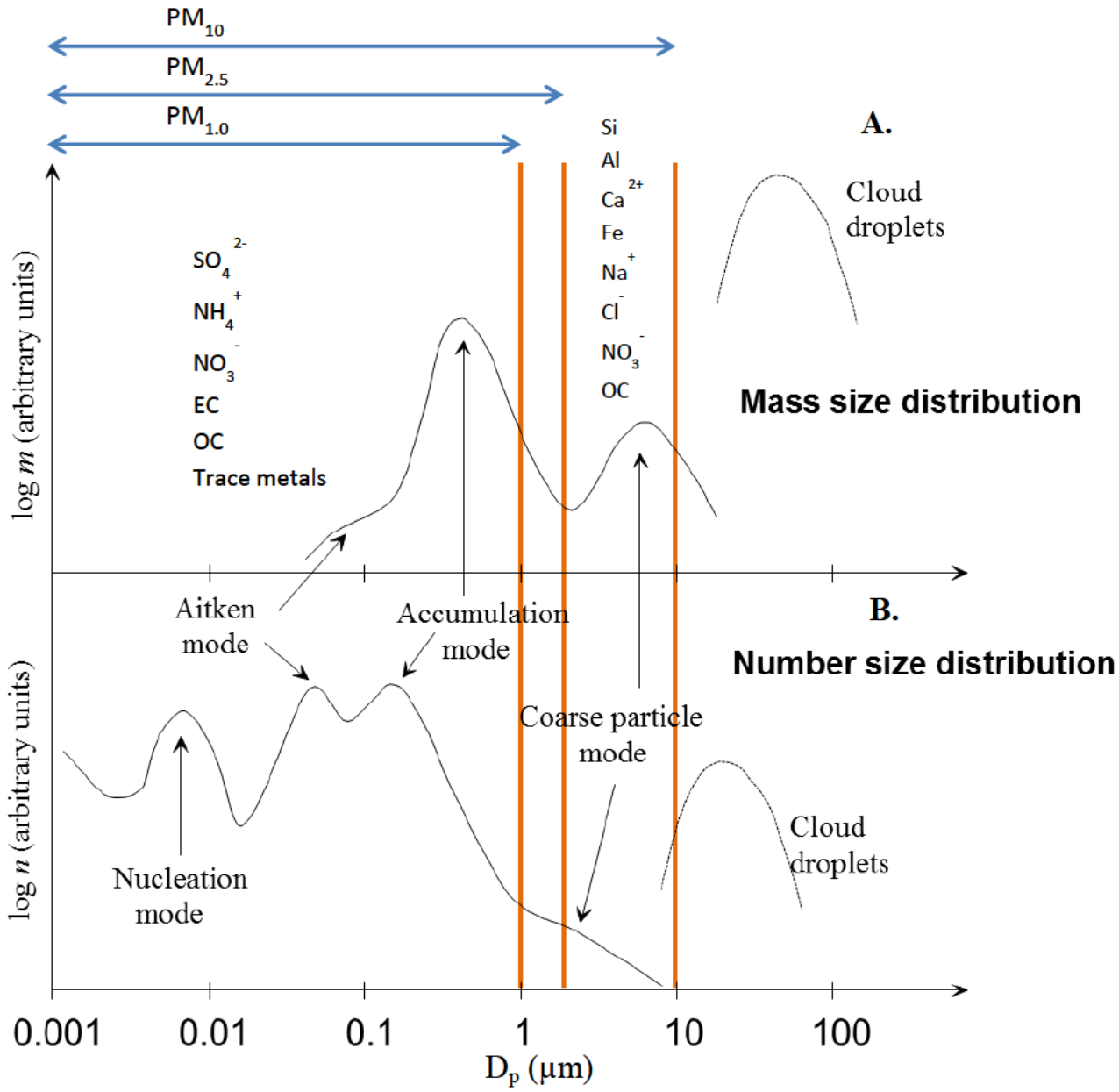

Figure 1. Typical mass (A) and number size distribution (B) of atmospheric particles and chemical composition in different particulate size ranges (Virkkula, 1999; Sillanpää *et al.*, 2005; 2006).

3.2.1 Chemical composition of particles

The chemical composition of particles in general depends on how they form and which sources emit them. Aerosol composition also varies according to the environment. Ultrafine particles (< 0.1 µm)

are mostly organic compounds and sulphates (Jimenez *et al.,* 2003). Fine particles are typically acidic or neutral (Kerminen *et al*., 2001) and consist of sulphate, ammonium, nitrate, elemental and organic carbon (EC/OC), and water (Pakkanen *et al.,* 2001). Coarse particles are typically basic and consist mainly of coarse sea-salt particles and crustal material (Kerminen *et al.,* 2001, Putaud *et al*., 2004). Nitrate, OC and trace metals are found in both fine and coarse fractions (Sillanpää *et al.,* 2006, **Paper II**).

Elemental carbon (black carbon, soot) originates only from combustion processes, whereas organic carbon is a complex mixture of different organic compounds originating from both natural (e.g., pollen, microbes, leaf wax) and anthropogenic sources (e.g., vehicles, fireplaces, paved road dust, cooking) (Schauer *et al*., 1996, Medeiros *et al*., 2006). Organic carbon is emitted either directly from sources (primary organic carbon) or forms in the atmosphere from precursor gases (secondary organic carbon). Several hundreds of organic compound have been identified in atmospheric particles such as alkenes, PAHs, carboxylic and aromatic acids, and a large group of organic macromolecular compounds (Graber and Rudich, 2006).

The inorganic fraction of fine particles is dominated by secondary ions such as ammonium, sulphate and nitrate, depending on the location (Matta *et al.,* 2003). In fine particles, ammonium nitrate usually results from the reaction of gaseous nitric acid and ammonia (Reaction 11). The reaction equilibrium depends on temperature and humidity; in cold conditions, ammonium nitrate is solid, but begins to dissociate as the temperature rises. Ammonium nitrate also exists as ions in aqueous droplets.

In coarse particles, however, nitrate forms from a reaction with sea salt (Reaction 12) or crustal material such as calcium carbonate (Finlayson-Pitts and Pitts, 2000):

$$CaCO_3\ (s) + 2HNO_3\ \ g) \rightarrow Ca\ NO_3)_2\ (s) + CO_2\ (g) + H_2O\ (l) \qquad (13)$$

In an abundance of ammonia, the reaction below converts sulphuric acid to ammonium sulphate (Seinfeld and Pandis, 2012):

$$2NH_4^+\ (aq) + SO_4^{2-}\ \ aq) \rightarrow\ NH_4)_2SO_4\ (s) \qquad (14)$$

Trace metals in particles originate mainly from different combustion processes such as oil, coal and wood combustion, as well as boilers, steel furnaces, smelters and waste incineration (Seinfeld and Pandis, 2012). Local sources strongly influence the concentrations levels of trace metals, but at certain locations, long-range transport dominates (Sillanpää *et al.*, 2006). Soil-related material is one of the main fractions in coarse particles containing Si, Ca, Fe, Al, K and Mn (Pakkanen *et al.,*

2001; Kupiainen *et al.,* 2005), whereas V and Ni are tracers of oil combustion, and As and Se, of coal burning (Chow and Watson, 2002).

3.3 Techniques for determining the gases and chemical composition of particles in air

The traditional method for measuring the chemical composition of particles is the filter sampling followed by chemical analysis. Cellulose, Teflon, glass and quartz fibre filters are most commonly used to collect particles. Cellulose filters impregnated with alkaline solution have been used to sample acidic gases (Huygen, 1963; Johnson and Atkins, 1975), and filters impregnated with acid to sample ammonia (Leuning *et al*., 1985; Anlauf *et al.*, 1988; Karakas and Tuncel, 1997). Open-face filter packs, where the front filter is used to collect particles and the following filters to measure gases, are currently used worldwide to measure air pollutants in monitoring networks such as the European Monitoring and Evaluation Programme (EMEP) (EMEP, 2007; Sickles *et al*., 1999). However, the time resolution with filter sampling is low (e.g., from several hours to days). In addition, filter sampling suffers from both negative and positive artefacts affected by volatilization and chemical reactions or retention on the filter material (e.g., Lipfert, 1994). Several studies have observed the evaporation of ammonium nitrate collected on filter media (Appel *et al.,* 1979; Hering and Cass, 1999). Also, in their studies of European conditions, Schaap *et al*. (2004) have found that Teflon is vulnerable to evaporation losses of ammonium nitrate, especially in dryer and warmer ambient conditions (Keck and Wittmaack, 2005). Additionally, the time resolution obtained with the filter method is still too long to detect the diurnal variations or short peak values needed to study atmospheric processes more closely.

Better time resolution for aerosol measurements have been obtained using the Particle-Into-Liquid Sampler (PILS) connected to an ion chromatograph (IC) (Weber *et al*., 2001, Orsini *et al.,* 2003) or an instrument for analyzing the concentration of water-soluble organic carbon (Kondo *et al.,* 2007). The PILS takes advantages of the steam-jet aerosol collector, SJAC (Khlystov *et al*., 1995; Simon and Dasgupta, 1995), which mixes ambient particles with saturated water vapour to produce droplets easily collected by inertial techniques and further analyzed with IC.

New instruments have been developed for semi-continuous measurements of both gases and aerosols. An URG-9000D Ambient Ion Monitor System (AIM URG Corporation, USA) can

provide measurements of acidic gases and ammonia in addition to the chemical composition of particles (Preunkert, 2012**)**. The instrument has served at an urban site in Beijing to measure hourly water-soluble inorganic ions in $PM_{2.5}$ and gaseous precursors (Hu *et al.*, 2014). The sample air is drawn through a plate diffusion denuder, which removes gases, and an Aerosol Super-Saturation Chamber collects particles. Ion chromatographs (Dionex) analyze both the collected particle and gas samples. Also the Dionex Gas Particle Ion Chromatography (GPIC) system, which measures concentrations of water-soluble inorganic aerosols, is based on this same principle (Godri *et al.,* 2009).

This study used the instrument for measuring AeRosols and Gases in Air (MARGA) (ten Brink *et al*., 2007), which measures the concentrations of water-soluble gases collected by diffusion in the liquid of a wet rotating denuder (Wyers *et al*., 1993). Particles are collected by condensation in the SJAC (Slanina *et al.,* 2001). An IC is used to analyze anions and cations from the gases and particles. In an earlier modification of the MARGA instrument, used at a rural site in the Amazon Basin (Trebs *et al.,* 2004), flow injection analysis (FIA) served to measure ammonium. In the Netherlands, MARGA served to monitor the size distribution of nitrate, ammonium, sulphate and chloride in aerosol (ten Brink *et al.,* 2007). In a clean background environment, a MARGA was used at an EMEP supersite in Scotland (Cape, 2007). The ability to measure both water-soluble aerosol and the precursor gas concentrations at a high time resolution has recently proved especially valuable for evaluating models, such as those for secondary inorganic aerosol formation (Schaap *et al*., 2011) and the gas-aerosol partitioning of ammonium nitrate (Aan de Brugh *et al.,* 2012).

4 EXPERIMENTAL

4.1 Measurement sites

All the measurements presented in this thesis were carried out in Finland in ambient air. Two of the stations, Kumpula and Hyytiälä, are SMEAR stations (Stations for Measuring Ecosystem–Atmosphere Relationships) that measure the relationship between the atmosphere and the surface in the boreal climate zone (Table 1). At the Kumpula station (SMEAR III), land–atmosphere and ecosystem relationships are measured in the urban background environment of Helsinki, at the university campus, close to the headquarters of the Finnish Meteorological Institute, FMI (Table 1, Fig. 2). All the other measurement sites of this study were rural background sites. Hyytiälä (SMEAR II) is a supersite dedicated to extensive long-term measurements. The other measurement sites of this study were EMEP (European Monitoring and Evaluation network) sites, such as Virolahti in south-eastern Finland. In addition, the EMEP sites of Ähtäri, Oulanka and Utö provided the long-term measurement data used in **Paper IV** (Fig. 2).

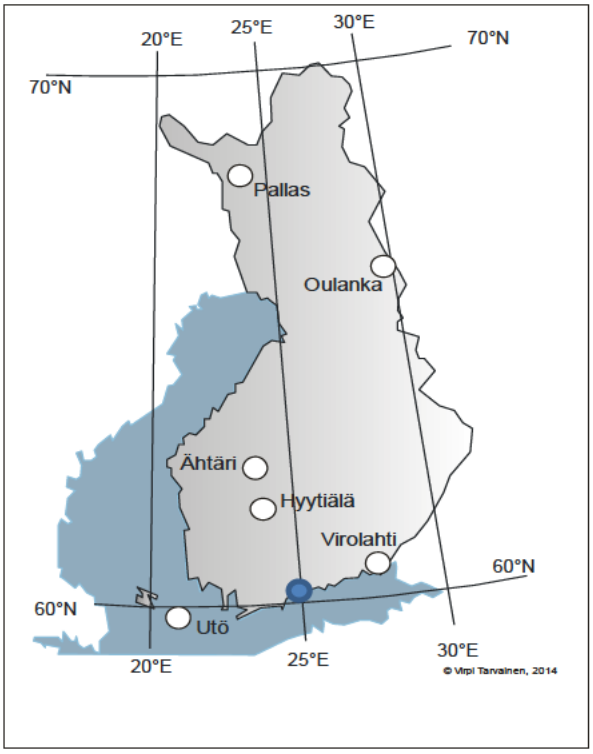

Figure 2. Locations of ambient measurement sites used in this thesis. Helsinki is indicated with a blue circle.

Table 1. Measurement sites and periods used in this thesis.

Site location	Site type	Measurement period	Paper
SMEAR III Helsinki, Kumpula	Urban background	1 November 2009 – 25 May 2010	III
SMEAR II Juupajoki, Hyytiälä	Rural background (Boreal forest)	21 June 2010 – 31 April 2011	V
Virolahti	Rural background EMEP station	15 September 1993 – 31 October 1994	I
		1 February 2006 – 28 February 2007	II
		1989–2013	IV
Ähtäri	Rural background EMEP station	1989–2013	IV
Oulanka	Rural background EMEP station	1991–2013	IV
Utö	Rural background EMEP station	1990–2013	IV

4.2 Online instruments

The instruments used in this study are listed in Table 2. The ambient particle number size distribution from 3 to 950 nm was measured with a Twin-Differential Mobility Particle Sizer (TDMPS, Aalto *et al*., 2001). The TDMPS consisted of two custom-built Hauke-type (Winklmayr *et al*., 1991) differential mobility analyzers (DMA) with closed loops for the sheath air flows connected to a Condensation Particle Counter (CPC). The first DMPS system used a TSI model 3025 CPC to measure particles between 3 and 50 nm, and the second system used a TSI model 3010 CPC to measure particles from 10 to 950 nm.

Section 4.3 discusses the online ion chromatograph MARGA (Monitor for AeRosols and Gases in Air). The Aerodyne Aerosol Mass Spectrometer (AMS) used in this study measures the chemical composition of aerosol particles using time-of-flight mass spectrometry (Jayne *et al.,* 2000; Jimenez *et al.,* 2003). An aerodynamic lens focuses aerosol particles of around 40–600 nm in size (Liu *et al.,* 2007) into a beam, and a 600°C thermal vaporization element flash-vaporizes all non-refractory compounds in the sample, and 70-eV electron impact ionization (EI) ionizes the resultant sample gas. Finally, a time-of-flight mass spectrometer produces a mass spectrum, and data inversion and

analysis reveal the aerosol concentration and composition. Although the time resolution achieved with AMS is much better than with ion chromatographs, AMS does not measure the gas phase.

Table 2. On-line instruments used for measurements in this thesis.

Method	Components measured	Manufacturer	Paper
TEI 43S –monitor	SO_2 fluorescence	Thermo-Environmental Inc.	I
TEI 43i tle –monitor	SO_2 fluorescence	Thermo-Environmental Inc.	III
TEI 49 –monitor	O_3	Thermo-Environmental Inc.	III
TEI 42S –monitor	NO_x	Thermo-Environmental Inc.	III
Twin DMPS	Size distribution	University of Helsinki	III
OA-CDRS	N_2O_5, NO_3 Absorption of NO_3 at 662 nm		IV
AMS	SO_4^{2-} , NO_3^-, NH_4^+	Aerodyne Research Inc.	V
MARGA	Cl^-, NO_3^-, SO_4^{2-},Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+-N (HCl), HONO, HNO_3, SO_2, NH_3	Applikon Analytical BV	III, IV,V

4.3 Online ion chromatograph

The main instrument used in this thesis was the semi-continuous online ion chromatograph, MARGA. The MARGA 2S ADI 2080 (Applikon Analytical BV, The Netherlands) consists of two identical sample boxes and one analytical box (**Paper III** and **V**). A PM_{10} inlet (Teflon coated, URG-2000-30DBQ) draws in ambient air at the flow rate of 2 m^3 h^{-1}. The air goes through the HDPE tube (Ø 1″), which is divided into two equal HDPE tubes (Ø 0.5″): one leading into the PM_{10} sample box (1 m^3 h^{-1}) and the other into the $PM_{2.5}$ sample box through a $PM_{2.5}$ cyclone (1 m^3 h^{-1}, Teflon-coated inlet, URG-2000-30ENB) (Fig. 3). The sample air is first drawn through the Wet Rotating Denuder (WRD), where water-soluble gases diffuse into the absorption solution; a Steam Jet Aerosol Collector (SJAC) then collects the particles (Fig. 5). Diluted hydrogen peroxide (10 ppm) serves as the absorption solution to prevent microbiological growth. Absorption solutions are drawn from the WRD and the SJAC into syringes (25 ml) in the analytical box (Fig. 4).

Each hour after filling the syringes, samples are injected into Metrohm anion 250 µl loo) and cation 500 µl loo) chromatogra hs with the internal standard (LiBr). A Metrosep C4 (100/4.0) cation column use 3.2 mmol l^{-1} HNO_3 eluent to separate cations, whereas a Metrosep A Supp 10 (75/4.0) column with Na_2CO3 - $NaHCO_3$ (7 mmol l^{-1}/8 mmol l^{-1}) eluent serve to separate anions. In the study in Hyytiälä the cation loop was later replaced by a concentration column (Metrosep C PCC 1 VHC/4.0) to improve the detection of small cation concentrations and the HNO_3 eluent was replaced with a methane sulfonic acid eluent (2.1 ml MSA in 10 l water) to get a better baseline for nitrate (**Paper V**). The column material used in the concentration column is spherical methacrylate with carboxylic groups. The concentration of the sample is based on the retention of the analytes measured in the concentration column material. After injecting the sample amount into the concentration column, we then eluate it from the column using counter flow and transport through the analytical column to the conductivity detector. In MARGA chemical suppressor (H_3PO_4 for regeneration) is used for the anions. We tested the repeatability of the sampling by running both of the sample boxes in parallel with no cut-off inlet (Table 3). Estimation of the detection limits was based on the ability of the MARGA software to identify peaks from the noise in the real air sample chromatograms. Blanks of the instrument were measured by installing filters in the sampling line before the denuder (an oxalic-acid-treated filter to remove ammonia, and a NaOH-treated filter to acidic gases) and subtracted from the results

Table 3. The detection limits and the repeatability (without using a concentration column) calculated from real air samples collected using the two parallel sample boxes of the MARGA instrument (1 Nov 2009 – 18 Jan 2010).

Compound	Detection limit µg m^{-3}	Repeatability %
HCl	0.02	30
HNO_2	0.03	3.3
SO_2	0.04	4.9
HNO_3	0.05	1.1
NH_3	0.05	3.9
Cl^-	0.02	4.5
NO_3^-	0.04	1.0
SO_4^{2-}	0.03	1.1
Na^+	0.02	1.2
NH_4^+	0.03	1.9
K^+	0.01	13.3
Mg^{2+}	0.01	8.7
Ca^{2+}	0.01	1.1

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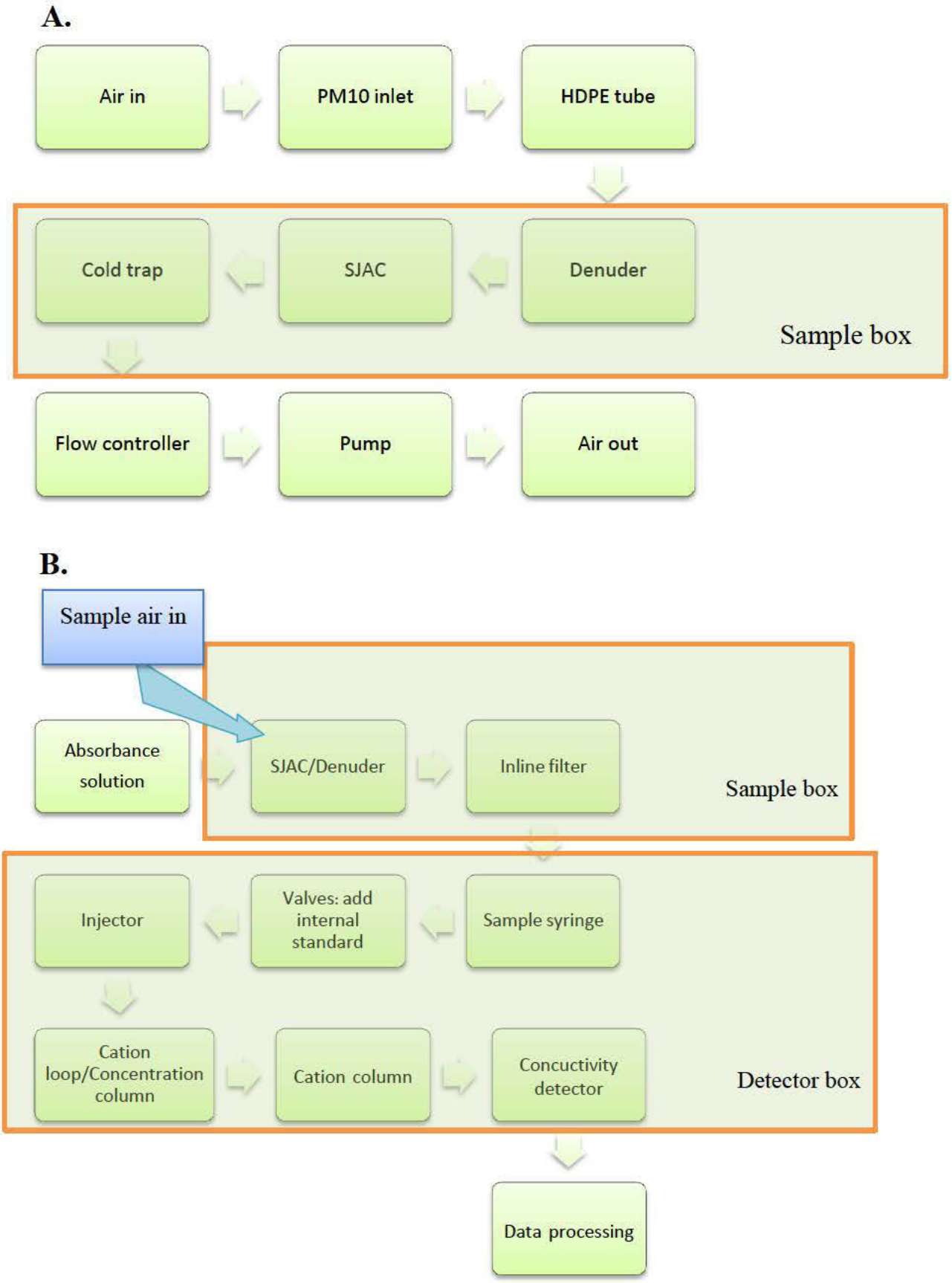

Figure 3. Air flow (A), sample uptake (B) and sample flow in the MARGA instrument.

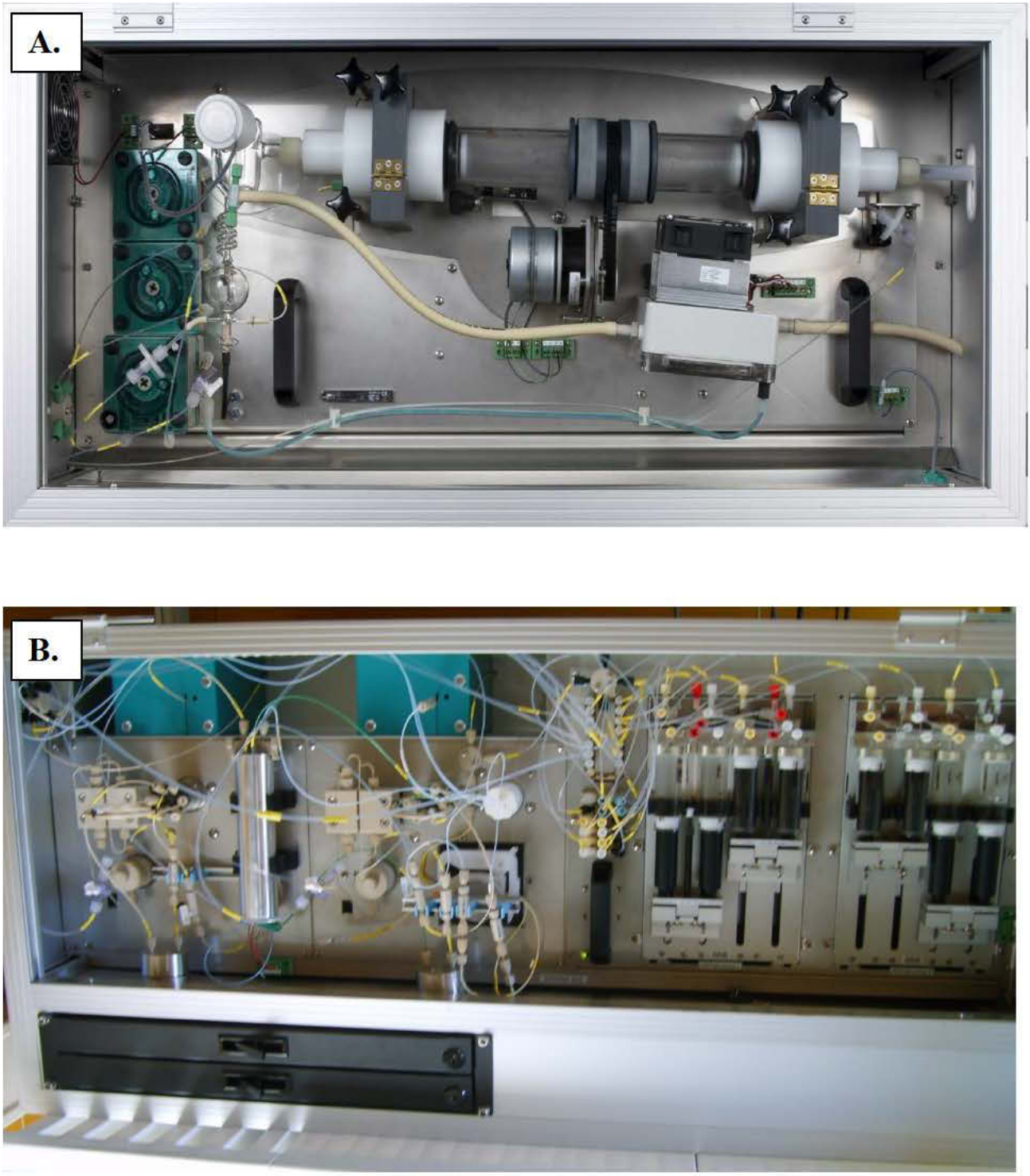

Figure 4. MARGA instrument: The sample box with the wet rotating denuder and the steam jet aerosol collector (A). The detector box (B) with its sample syringes, cation and anion chromatographs.

Figure 5. The steam jet aerosol collector (SJAC) of the MARGA.

4.4 Sampling methods

The studies used three sampling methods: sampling on filters, passive sampling, and sampling in the absorption solution. Particulate matter in PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ fraction was collected on PTFE membrane filters (47 mm, 3.0 µm, FS, Fluoropore TM, Millipore, Ireland) for mass determination (**Paper II**). A Mettler Toledo UMT2-balance (precision of 1 µg; Mettler Toledo GmbH, Switzerland) served to weigh the filters before and after the sampling. After weighing, certain filters were selected for chemical analysis (**Paper I**).

EMEP filter packs (FP) (Huygen, 1963, Johnson and Atkins, 1975) and filter samplers with different cut-offs were used to test different measurement methods (Table 4). A single-stage FP with one cellulose filter impregnated with oxalic acid was used to measure (NH_3+NH_4^+)-N. The two-stage FP consisted of the Teflon front filter for particles and a NaOH-impregnated filter for collecting acidic gases (e.g., SO_2, HNO_3). After the Virolahti comparison (**Paper I**), the two-stage FP and the single-stage FP were replaced with a three-stage FP. The three-stage FP, with its Teflon front filter for particles, impregnated filter for acidic gases, and final filter for ammonia, was used at the background stations (**Papers I and V**).

Table 4. Sampling methods used in this thesis.

Method	Flow L min^{-1}	Components measured	Collecting media	Time resolution	Paper
1-stage FP	17	$(NH_4^+ + NH_3)$-N	Oxalic acid-impregnated cellulose filter[1]	24 h	I,VI
2-stage FP	17	SO_4^{2-}, NO_3^--N SO_2, HNO_3^--N	Cellulose filter[1] NaOH-impregnated cellulose filter[1]	24 h	I
3-stage FP	17	Cl^-, SO_4^{2-}, NO_3^--N Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+-N SO_2 HNO_3-N NH_3-N	PTFE[2] NaOH-impregnated cellulose filter[1] Oxalic acid-impregnated cellulose filter[1]	24-72 h	I, V I, V I, V I, V I, V
Absorption solution	2	SO_2 SO_4^{2-}	0.3% H_2O_2 solution Cellulose filter[1]	24 h	I
Absorption solution	2	SO_2 SO_4^{2-}	0.3% H_2O_2 solution PTFE[2]	2 weeks	I
Passive sampler		SO_2	NaOH-impregnated cellulose filter[1]	2 weeks 1 month	I I
PM_{10}[3]	38	Mass Ions Trace elements PAH	PTFE[2]	24 h	II II II II
PM_{10}[3]	17	Ions	PTFE[2]	24 h	III
$PM_{2.5}$[4]	35	Mass Ions Trace elements PAH	PTFE[2]	24 h	II II II II
$PM_{2.5}$[3]	17	Ions	PTFE[2]	24 h	III
$PM_{1.0}$[5]	18	Mass Ions Trace elements PAH	PTFE[2]	24 h	II II II II

[1] Whatman 40-filter paper, Ø 47 mm, except for absorption solutions, $PM_{1.0}$ and passive sampler, Ø 25 mm
[2] PTFE membrane filter (Ø 47 mm, 3.0 µm, FS, Fluoropore TM, Millipore, Ireland)
[3] Digitel
[4] MCZ
[5] IVL PModel S1

The first paper also included old absorption solution methods in order to evaluate the quality of the old background monitoring SO_2 data, as well as passive samples used in Sweden by IVL (Institut för Vatten och Luftforskning), where NaOH-treated Whatman cellulose filters (Ferm, 1991; Ferm and Rodhe, 1997; Ferm M. and Svanberg, 1998) are used to collect SO_2.

Both PM_{10} and $PM_{2.5}$ filters as well as EMEP filter packs (FP) were used (**Papers II and V**) to collect samples for chemical analysis in order to validate the MARGA instrument.

4.5 Chemical analyses

To determine the ions, filters (or filter subsamples) used to collect particulate matter were extracted in ultrapure water, then filtered and analyzed with an IC. We also used an IC to analyze the water extracts of the impregnated EMEP filters (for acidic gases and ammonia) and the filters of the passive samplers (Table 5). We then used the Waters ICs (Waters 501 pump, Waters 431 Detector) to analyze the cations and anions from all the filter extracts. The MARGA instrument used Metrohm ICs for anions and cations (Table 5). For more detailed descriptions of the procedures, see **Papers I–V** and the EMEP Manual (2007).

Table 5. The columns and eluents used for measuring ions.

Sampling system		Ions	Column	Eluent
Teflon filter	Particles	Cl^-, NO_3^-, SO_4^{2-}	Waters IC-Pak A HR	borate/gluconate
NaOH-impregnated filter	SO_2, HNO_3	SO_4^{2-}, NO_3^-	IonPac AS9-HC	Na_2CO_3 , 9 mmol
Teflon filter	Particles	Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	IC-Pak C M/D	EDTA-HNO3
Oxalic acid-impregnated filter	NH_3	NH_4^+	Waters IC-Pak C	Na_2EDTA-HNO_3
MARGA	Particles and gases	Cl^-, NO_2^-, NO_3^-, SO_4^{2-}	Metrosep A Supp 10	$NaCO_3$/$NaHCO_3$ eluent 7 mmol l^{-1} / 8 mmol l^{-1}
MARGA	Particles and gases	Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Metrosep C 4 100	HNO_3, 3.2 mmol l^{-1} MSA, 3.2 $mmol^{-1}$

For the trace element analysis, we used a solution of HF and HNO_3 in an ultrasonic bath to extract the Teflon filter samples (Jalkanen and Häsänen, 1996). Using Rh as an internal standard and an inductively coupled plasma mass spectrometer (ICP-MS; Perkin Elmer Sciex Elan 6000) at FMI, we analyzed the samples for eleven different trace elements (Al, As, Cd, Co, Cu, Pb, Mn, Ni, Fe, Zn and V).

To extract the PAH samples, we used dichloromethane with Soxhlet extraction, dried with Na_2CO_3 and concentrated with a rotary evaporator and nitrogen flow. We used a gas chromatograph (Agilent 6890N) with an HP-5MS column 30 m, i.d. 0.25 mm, film thickness 0.25 μm) and a mass spectrometer (Agilent 5973) to analyze the samples. For the calibration, PAH solution (Supelco EPA 610 Polynuclear Aromatic Hydrocarbon mix) with certified concentrations served as external standards, and deuterated PAH compounds (Dr Ehrenstorfer, internal standard mix) as internal standards.

5 RESULTS AND DISCUSSION

5.1 Comparison of the methods

5.1.1 Sulphur dioxide and sulphate comparisons

We used various sampling techniques, including filters, SO_2-online monitors, absorption solutions, passive samplers and MARGA, to measure sulphur dioxide concentrations (**Papers I, II, III and V**). Comparisons which included the MARGA instrument appear in Chapter 5.1.2. Below is a summary of the comparisons:

- The SO_2 concentrations from the monitor and filter methods (see Table 4) agreed well: the monitor data set was about 6% lower than that from the EMEP filters (FP vs. monitor regression line $y = 0.94x + 0.03$, $r^2 = 1.00$, n = 164, **Paper I**).
- The absorption solution method (daily sampling) and the two-stage FP showed a considerable bias, especially at lower SO_2 concentrations; nevertheless, the average with the absorption solution over the entire test period (6 months) was only 4% higher. (regression line FP vs. abs. $y = 0.89x + 0.47$, $r^2 = 0.99$, n = 165). According to **Paper I**, the absorption solution method cannot be recommended for use at sites with low SO_2 concentrations.
- The passive sampler agreed quite well with the two-stage FP, although the concentrations of the passive sampler were about 10% higher (regression line $y = 1.09 x + 0.10$, $r^2 = 1.00$, n = 26). Passive samplers can be used to replace the absorption-solution method for monitoring average SO_2 trends at background stations (**Paper I**).
- The SO_2 and SO_4 values measured with the two-stage and three-stage FPs (n = 28) showed no significant differences. This implies that three-stage FPs can replace two-stage and single-stage FPs (**Paper I**).
- The sulphate concentrations measured with the front filter of absorption solution inline filter were considerably lower than those measured with the two-stage FP. Any use of the old sulphate data (e.g., for long-term trend analysis) should take this into account (**Paper I**).

Of the methods used in this study, the SO_2 monitors and the EMEP three-stage FP are still used in background air monitoring. Passive samples are not currently used at background sites due to their long sampling times. However, because of the implementation of Directive 2008/50/EC to measure

the chemical composition of $PM_{2.5}$, discussion about harmonizing EMEP filter methods and the $PM_{2.5}$ filter method are underway. EMEP filter packs commonly use low blank Teflon filters, but quartz filter material has been chosen for use in validation tests of the European standard Ambient air quality - Guide for the measurement of anions and cations in $PM_{2.5}$. However, both the filter materials have artefacts in sampling NH_4NO_3.

5.1.2 Comparison of the MARGA with the other techniques

For validation purposes, the MARGA instrument was run parallel with filter sampling (**Papers III, V**). In Helsinki, the MARGA instrument was compared to the daily PM_{10} filter method, and in Hyytiälä, to the EMEP filter pack method with a two- to three-day sampling period (Table 6). In addition, we compared concentrations of MARGA to those of the SO_2 monitor and AMS (Table 6).

Table 6. Regression slopes y(MARGA) = a·x(comparison method) + b, with coefficients of determination (r^2). MARGA was compared to the PM_{10} filter method in Helsinki during winter-spring, and with the EMEP filter pack in summer-winter in Hyytiälä using both ordinary loops (500 µl for the cations, 250 µl for the anions) and a concentration column for the cations.

	Helsinki PM10 vs. MARGA	r^2	Hyytiälä FP vs. MARGA with loop	r^2	Hyytiälä FP vs. MARGA with concentration column	r^2
SO_2			*y = 0.98x + 0.13*	*0.89*		
HNO_3			*y = 0.50x + 0.07*	*0.70*		
NH_3			*y = 1.00x + 0.07*	*0.79*		
Cl^-	*y = 0.72x + 0.03*	*0.83*				
NO_3^-	*y = 0.90x + 0.46*	*0.93*	*y = 1.31x + 0.08*	*0.93*		
SO_4^{2-}	*y = 0.85 + 0.24*	*0.98*	*y = 1.08x + 0.05*	*0.90*		
Na^+	*y = 0.49x − 0.03*	*0.55*	*y = 1.50x – 0.03*	*0.70*	*y = 0.88x – 0.01*	*0.95*
NH_4^+	*y = 0.91x − 0.30*	*0.83*	*y = 1.23x + 0.15*	*0.61*	*y = 1.19x + 0.04*	*0.83*
K^+	-	-	*y = 1.51x – 0.02*	*0.75*	*y = 1.00x*	*0.90*
Mg^{2+}	*y = 3.03x − 0.02*	*0.69*	*y = 3.39x + 0.01*	*0.86*	*y = 0.73x*	*0.85*
Ca^{2+}	*y = 3.03x + 0.09*	*0.86*	*y = 2.95x + 0.07*	*0.97*	*y = 0.89x*	*0.62*

The sulphate and sulphur dioxide concentrations measured with all the methods included (the filter methods, the monitor, the AMS, and the MARGA) showed good agreement. The sulphate

concentrations of the MARGA were about 7% lower in Helsinki (**Paper III**) and about 8% higher in Hyytiälä (**Paper V**) than those of the filter method. Also, the AMS sulphate data (cut-off 1 μm) fit well with the MARGA (cut-off 2.5 μm, $y = 1.01x - 0.25$, $r^2 = 0.92$), indicating that sulphate was present mainly in submicron particles (**Paper V**). For SO_2, the MARGA showed slightly higher concentrations than did the EMEP filter in Hyytiälä (**Paper V**) and lower (about 10%) than did the monitor in Helsinki (**Paper III**). This indicates that all three methods (i.e., the monitor, the MARGA and the filter pack method) are suitable for measuring SO_2 concentrations.

In Helsinki (**Paper III**), ammonium concentrations measured with the MARGA were lower (23%) than those with the filter method, but in Hyytiälä, they were considerably higher (about 30%). The difference decreased in Hyytiälä after installing a concentration column: the ammonium concentrations with the MARGA were about 20% higher than those with the filter method. On the other hand, the ammonium concentrations with the MARGA (with $PM_{2.5}$ inlet) were somewhat higher than with the AMS, indicating that a considerable fraction of the ammonium was in particles larger than 1 μm (**Paper V**). One source of greater measurement uncertainty for NH_4^+ was that Na^+ was not totally resolved from NH_4^+, so integrating the peaks close to each other in the best possible way with the MARGA software proved impossible. However, the NH_3 concentrations measured with the MARGA agreed well with those of the filter method (**Paper V**).

With the MARGA, the nitrate concentrations measured were considerably higher and the HNO_3 concentrations were considerably lower than with the filter method, indicating that some nitrate had evaporated from the Teflon front filter and penetrated the impregnated filter (**Paper V)**. However, the sum ($HNO_3 + NO_3$) measured with the filter and the MARGA agreed well ($y = 0.97 + 0.09$, $r^2 = 0.89$). Because HNO_3 attaches easily to surfaces, some inlet losses may have occurred (Rumsey, 2013). The nitrate concentrations of the AMS were much lower than those of the MARGA, and the considerable scatter may partly stem from the different cut-offs of the instruments. It is also worth noting that the NO_3 blank, which was subtracted from all the MARGA results, may not have remained constant throughout the entire measurement period possibly leading to inaccuracies (**Paper V**).

With regard to potassium, magnesium and calcium, agreement with the filter method improved remarkably after adding a concentration column (**Papers III, V**). With an ordinary loop, the MARGA yielded concentrations that were three-fold higher than with the filter. Replacing the loop with a concentration column led to much better agreement between the two methods (Table 6).

5.2 Concentration levels and temporal variations of inorganic gases

5.2.1 Trends in background air

The EMEP FP has served to measure sulphur dioxide and reduced nitrogen (ammonia and ammonium) with 24-h time resolutions at Finnish background stations since the 1970s. Recent years have witnessed a decreasing trend in SO_2 (Fig. 6), and emissions of reduced nitrogen in Europe decreased by 20% between 1990 and 2005 (Aneja *et al.,* 2008). Trend calculations performed (**Paper IV**) for concentrations of reduced nitrogen measured at Finnish EMEP stations during 1990–2007 with the MAKESENS software (Salmi *et al.,* 2002) showed that concentrations of reduced nitrogen have decreased in southern and central Finland between 1990 and 2007. We have studied the factors contributing to this decrease in greater detail using trajectory analysis for the data of two background stations, Utö and Oulanka, (**Paper IV**). The trajectories indicate that ammonium concentrations from southern to western sectors were dominant at both the sites. In Utö, the ammonium concentrations measured decreased during the study period in air from the southwest and east. In addition, the frequency of winds from the west decreased. In Oulanka, the concentrations showed no decrease in any sector, but the air transport from the west shifted to the north, thereby decreasing the concentration of reduced nitrogen. In Finland, changes in European emissions patterns and in the transport pathways of air masses strongly affected the ammonium concentrations. In 1990-2013, annual mean concentrations of ammonia decreased significantly in all sites studied: Ähtäri, Utö, Virolahti and Oulanka (Fig. 6). The ratio of reduced nitrogen to sulphate increased in all sites except Ähtäri (Fig. 6), showing that the concentration of sulphate decreased more rapidly and, consequently, atmospheric particles in those areas have become less acidic. Figure 6 also shows how important it is to choose a measurement site uninfluenced by local conditions. In the 1990s, elevated concentrations of ammonia were detected in Virolahti because of local emissions, later the site was relocated.

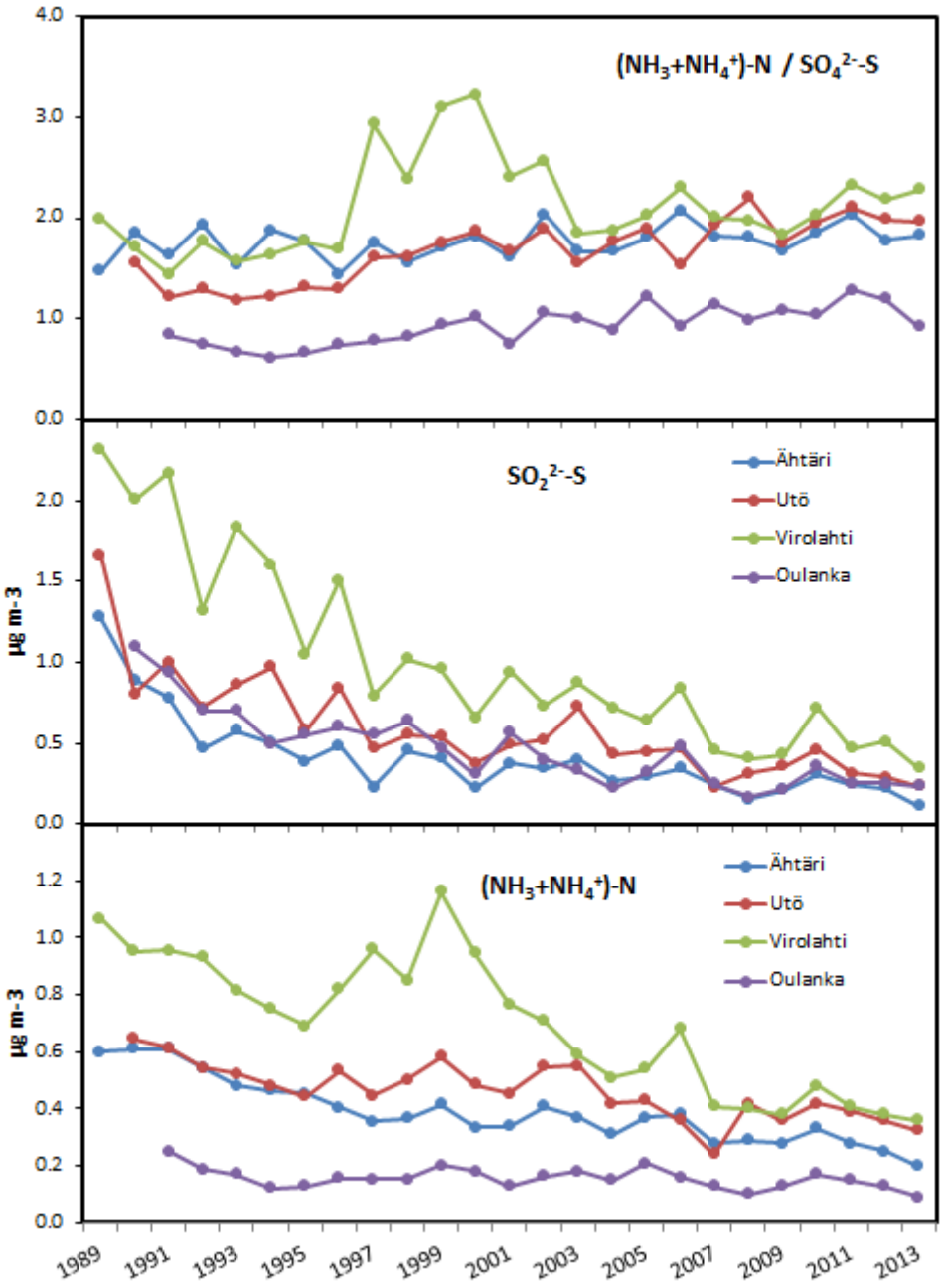

Figure 6. The ratio of reduced nitrogen to sulphate, sulphur dioxide (S µg m^{-3}) and reduced nitrogen (N µg m^{-3}) at Finnish EMEP background sites from 1989 to 2013.

5.2.2 Concentration levels in Helsinki and Hyytiälä and their seasonal variation

An online ion chromatograph MARGA was set up in 2010 to achieve better time-resolution data on inorganic gases and particles. MARGA enables the measurements of gas and aerosol phases separately, which is not possible with the other techniques used. We measured inorganic gases (HCl, HONO, SO_2, HNO_3 and NH_3) with the MARGA instrument in Helsinki (**Paper III**) and Hyytiälä (**Paper V**). When comparing the concentration levels at these two sites, we must bear in mind that the measurements were performed during different time periods – in Helsinki during winter-spring 2009-2010 and later in Hyytiälä – so annual variations in temperature and other environmental conditions already influence the concentrations. As expected, the concentrations of all the acidic gases were higher in Helsinki than in Hyytiälä, which has fewer anthropogenic sources (Table 7). The data on hydrochloric acid was excluded, because concentrations of HCl were usually below or close to the detection limit of the instrument, especially in Hyytiälä. In Helsinki concentration of sulphur dioxide were about three to five times higher than in Hyytiälä. The surroundings of Helsinki reflect SO_2 emissions from sources of fossil fuel combustion in power plants, heating plants and ships. During the colder winter periods, the increase in concentrations of SO_2 in both the city (1.3 ppb) and Hyytiälä (0.5 ppb) was most likely due to increased heating emissions and the longer lifetime of SO_2: in cold and dark conditions, SO_2 can travel over longer distances before undergoing oxidation.

As expected, concentrations of HONO and HNO_3 were higher in Helsinki, which has typical urban traffic emissions of NO (Table 7). In the atmosphere, NO oxidizes to NO_2, which further oxidizes to HONO and HNO_3. In Hyytiälä, the concentrations of HNO_3 measured in summer (mean 0.10 ppb) were slightly higher than in other seasons (0.06–0.07 ppb), following the amount of sunlight at the northern latitudes. Nitrous acid dissociates in the presence of sunlight, which explains why the concentrations of HONO in Helsinki were much higher in the dark winter period than in spring (Reaction 4). In Hyytiälä, however, the concentration of HONO was highest in the summer period, indicating possible local emission sources from soil, as Su *et al*. (2011) have suggested.

In winter and spring, the concentrations of ammonia were higher in Helsinki 0.3 ppb) than in Hyytiälä (0.05 ppb). Likely because urban environments have more sources of ammonia, including industries, humans, landfills and vehicles equipped with catalytic converters. In the warm summer months, ammonia concentrations increased remarkably in Hyytiälä (0.47 ppb), possibly because, in addition to increased volatility as a function of temperature, agricultural and biogenic emissions are stronger in summer.

5.2.3 Diurnal cycles of N-containing gases in Helsinki and Hyytiälä

In Kumpula (**Paper III**), we observed a diurnal cycle in spring (March–May, 2011) not only for nitric acid, but also for nitrate in PM_{10}. The HNO_3 concentration reached a minimum in the morning between 07:00 and 09:00 (local time) and a clear maximum between 12:00 and14:00, as well as the maximum average concentration of nitrate two hours earlier, at 10:00. These diurnal cycles resembled those observed in Zürich (Fisseha *et al.*, 2006): the concentration of nitrate peaks a few hours earlier than that of HNO_3. The time lag can be attributed to the temperature-dependent partitioning of ammonium nitrate between the gas and aerosol phases (e.g., Fisseha *et al*., 2006). In winter, the HONO concentration was higher in the daytime and lower at night, reaching a minimum between 4:00 and 5:00. In spring, concentrations rose in the early mornings, reaching a maximum between 7:00 and 8:00, and declined in the afternoons reaching a minimum between 13:00 and 16:00. This again resembles the cycle observed in Zürich in March 2003, where the HONO concentration reached a maximum at about 09:00 and decreased throughout during the day until it reached a minimum at 17:00 (Fisseha *et al*., 2006). The times of the diurnal maxima in the studies differed somewhat, because the diurnal cycles and the amount of sunlight depend on both the site and the time of the year.

In Hyytiälä, we found no clear diurnal cycle for any of the gases measured in the winter period (**Papers V**). The summer, however, showed a clear diurnal cycle for both HONO and HNO_3. Nitrous acid had its highest values before sunrise, but as the day progressed, however, concentrations remained low and began rising again late in the evening (Fig. 7). The cycle for HNO_3 was the opposite: the lowest concentrations were measured during the early morning hours and rose throughout the day, peaking in the afternoon and falling again towards the midnight. The cycle for HONO resulted from the above-mentioned photochemical dissociation of HONO, which yielded OH radicals (Reaction 4) needed to form HNO_3 (Reaction 9).

During the cold period, ammonia concentrations remained low, and there was diurnal variation neither in Helsinki nor in Hyytiälä. By April, diurnal variation had begun, but it was weak. Summertime measurements were performed only in Hyytiälä, where NH_3 showed clear diurnal variation, reaching the maximum in the afternoon. The concentrations decreased in the evening, but began rising again in the morning. In the autumn, the diurnal variation weakened with the falling air temperatures (Fig. 8). Ammonium, however, showed no diurnal cycle, so the cycle cannot be explained by the dissociation of ammonium nitrate (Reaction 11). The observed cycle suggests that ammonia that settled on leaf surfaces and vegetation during the cooler night time may be re-emitted

as the temperature rises again after sunrise, or the cycle results from emissions from plants and trees. Vegetation emits ammonia when exposed to air with an ammonia concentration lower than the compensation point, which is temperature dependent (Farquhar *et al*., 1980). Our results suggested that ammonia concentrations depend exponentially on air temperature, the increase with temperature being strongest in dry conditions (**Paper V**). The temperature dependence of NH_3 in this study agreed with earlier findings. Warm weather increases NH_3 volatilization (Monteny and Erisman, 1998) as well as emissions from vegetation. An increase in the leaf temperature of oilseed rape from 10 to 35°C led to an exponential increase in NH_3 emissions (Husted and Sjoering, 1996).

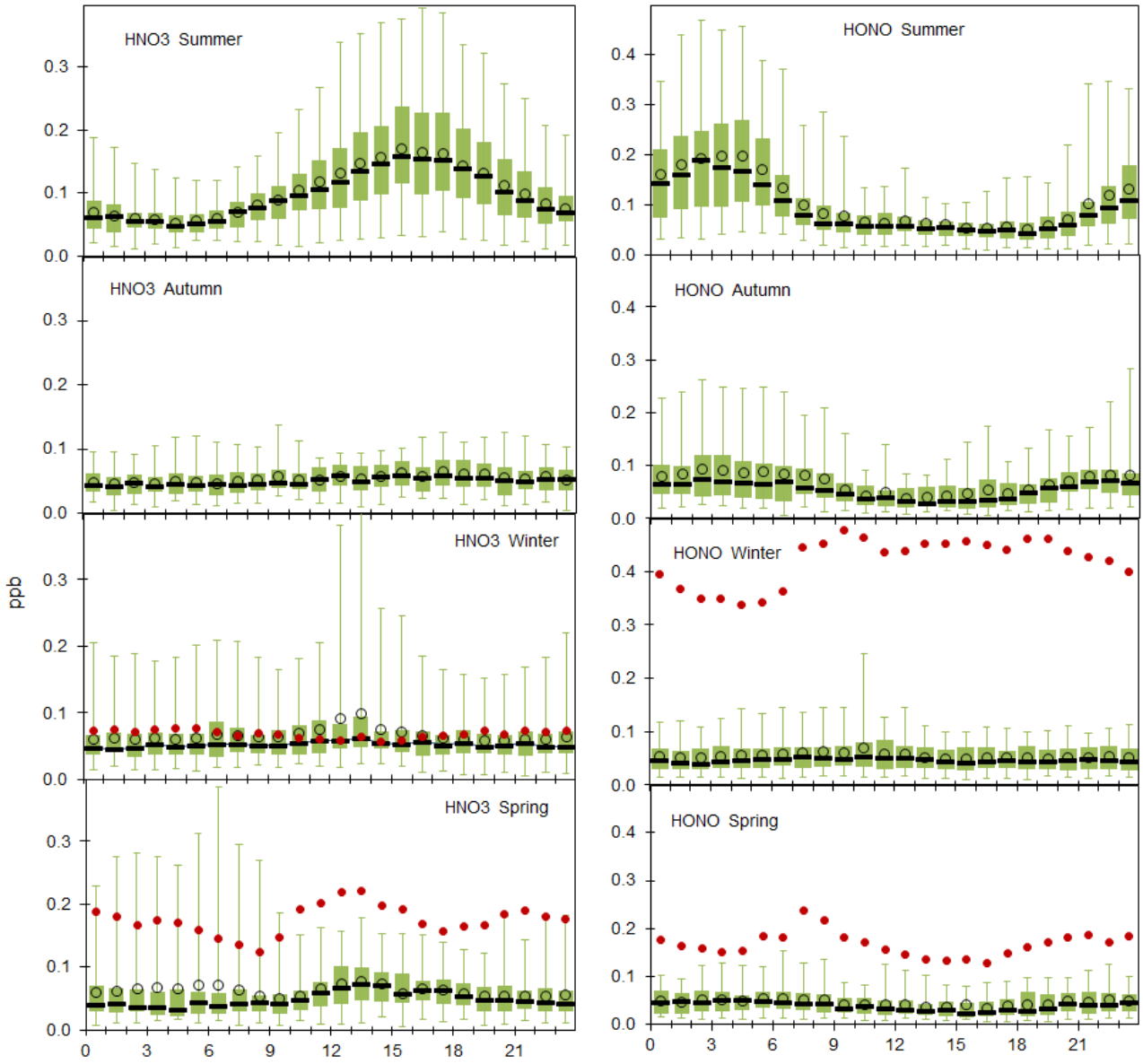

Figure 7. Diurnal cycles of nitric acid and nitrous acid measured in Hyytiälä (median values: circles) in 2011–2012 and in *Kumpula* (median values: *red* circles) in winter and spring 2010–2011. The green box represents the 25th to 75th percentile range, the bars represent the 90% range (5th and 95th percentiles), and the horizontal line is the median of the hourly averaged data measured in Hyytiälä.

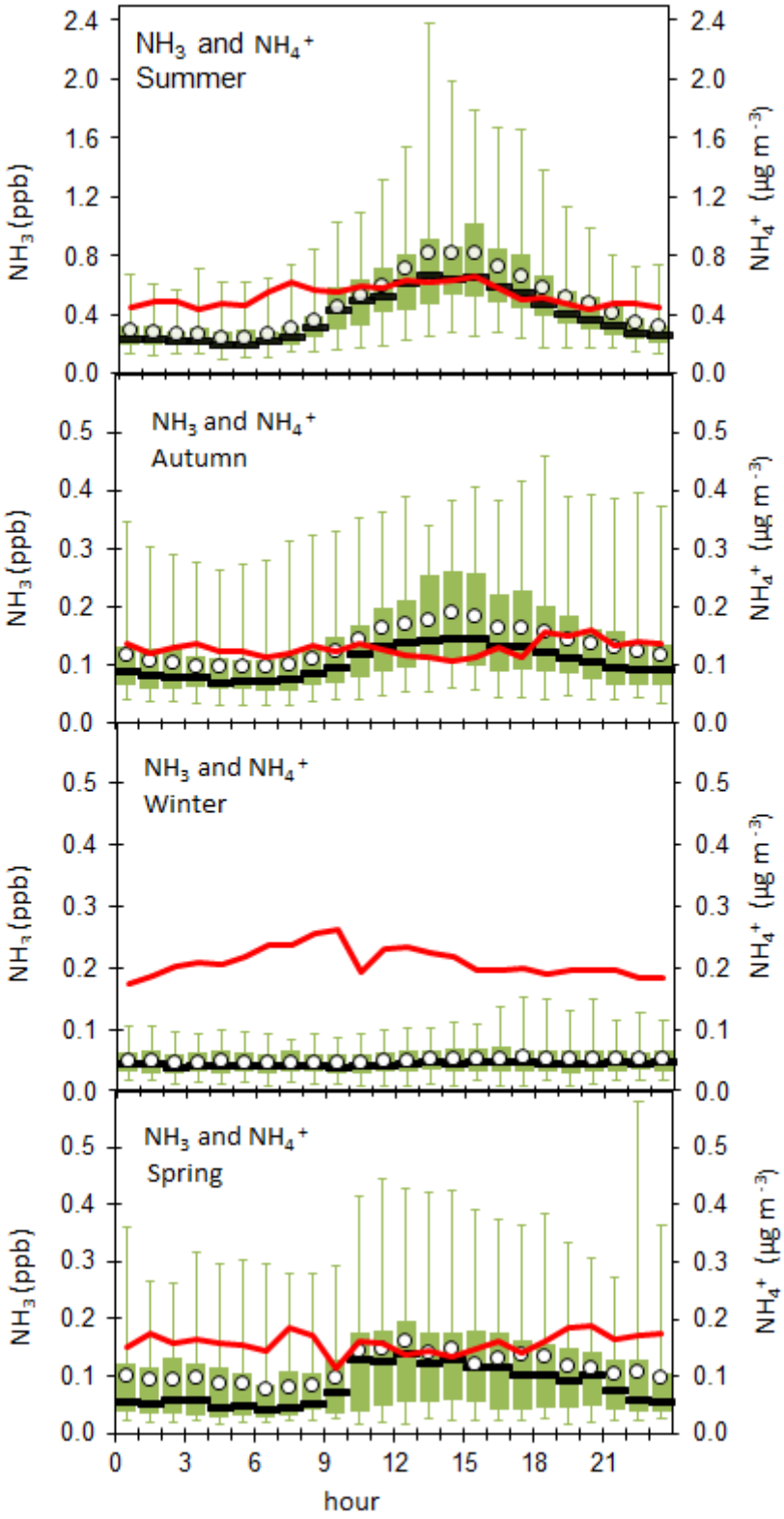

Figure 8. Diurnal cycle of ammonia measured in Hyytiälä in 2011–2012. The green box represents the 25th to 75th percentile range; the bars, the 90% range (5th and 95th percentiles); the horizontal line, the median; and the circle, the averages of the hourly averaged data for each hour. The red lines represent the median ammonium concentrations (µg m^{-3}) in the PM_{10} fraction.

Table 7. Concentrations of inorganic gases (ppb) in Hyytiälä and Helsinki (average ± standard deviation and median) calculated from the MARGA data. Measurements were conducted in Hyytiälä in June 2010 – May 2011 and in Helsinki (19 Jan 2010 – 25 May 2010).

	Hyytiälä summer mean ± SD	median	autumn mean ± SD	median	winter mean ± SD	median	spring mean ± SD	median	Helsinki winter mean ± SD	median	Helsinki spring mean ± SD	median
HONO	0.11 ± 0.09	0.07	0.07 ± 0.05	0.06	0.06 ± 0.03	0.048	0.05 ± 0.03	0.04	0.45 ± 0.33	0.37	0.19 ± 0.14	0.15
SO_2	0.18 ± 0.24	0.11	0.08 ± 0.09	0.06	0.49 ± 0.94	0.237	0.16 ± 0.26	0.09	1.32 ± 1.73	0.65	0.76 ± 1.00	0.47
HNO_3	0.10 ± 0.07	0.08	0.06 ± 0.03	0.05	0.07 ± 0.05	0.053	0.06 ± 0.06	0.05	0.13 ± 0.12	0.09	0.22 ± 0.19	0.15
NH_3	0.47 ± 0.36	0.36	0.14 ± 0.09	0.12	0.05 ± 0.03	0.045	0.09 ± 0.10	0.06	0.25 ± 0.44	0.01	0.28 ± 0.41	0.14

Table 8. The concentration of inorganic ions (µg/m^3) in PM_{10} in Virolahti in 2006 (Episode 1 the fire days: 25 Apr–7 May and Episode 2, the fire days, 2–3, 8–15 and 21–22 August), Hyytiälä 2010-2011 and Helsinki (19 Jan 2010 – 25 May 2010). Virolahti and Helsinki results are calculated from filter data and Hyytiälä results from MARGA-data (the filter pack results are in brackets).

	Virolahti Episode 1 mean + SD	Episode 2 mean + SD	summer mean + SD	winter mean + SD	Hyytiälä summer mean + SD	autumn mean + SD	winter mean + SD	spring mean + SD	Helsinki winter mean + SD	spring mean + SD
Cl^-	0.02 ± 0.01	0.04 ± 0.03	0.03 ± 0.05	0.23 ± 0.28	0.05 ± 0.10 (< 0.01)	0.09 ± 0.17 (0.07 ± 0.07)	0.04 ± 0.11	0.14 ± 0.21	0.05 ± 0.03	0.23 ± 0.24
NO_3^-	1.05 ± 0.67	0.45 ± 0.36	0.33 ± 0.31	0.47 ± 0.24	0.33 ± 0.23 (0.16 ± 0.09)	0.38 ± 0.53 (0.23 ± 0.23)	0.47 ± 0.45	0.44 ± 0.54	2.06 ± 2.46	1.53 ± 2.12
SO_4^{2-}	3.25 ± 1.89	1.95 ± 0.84	1.97 ± 1.59	0.94 ± 0.53	1.34 ± 1.02 (1.26 ± 0.71)	0.77 ± 0.76 (0.71 ± 0.55)	1.39 ± 1.38	0.70 ± 0.49	3.48 ± 1.26	1.63 ± 1.08
Na^+	0.07 ± 0.03	0.05 ± 0.02	0.17 ± 0.15	0.27 ± 0.20	0.05 ± 0.09 (0.09 ± 0.07)	0.10 ± 0.14 (0.11 ± 0.11)	0.19 ± 0.15	0.25 ± 0.16	0.16 + 0.10	0.25 + 0.21
NH_4^+	1.21 ± 0.77	0.70 ± 0.35	0.57 ± 0.48	0.27 ± 0.18	0.55 ± 0.47 (0.33 ± 0.19)	0.27 ± 0.35 (0.20 ± 0.19)	0.38 ± 0.43	0.28 ± 0.41	1.23 ± 0.65	0.76 ± 0.79
K^+	0.28 ± 0.10	0.16 ± 0.07	0.05 ± 0.02	0.05 ± 0.03	0.07 ± 0.17 (0.06 ± 0.05)	0.05 ± 0.06 (0.05 ± 0.03)	0.07 ± 0.08	0.04 ± 0.07	0.14 ± 0.06	0.06 ± 0.04
Mg^{2+}	0.04 ± 0.01	0.02 ± 0.01	0.03 ± 0.03	0.03 ± 0.02	0.10 ± 0.09* (0.03 ± 0.02)	0.02 ± 0.02 (0.02 ± 0.01)	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.02	0.03 ± 0.02
Ca^{2+}	0.26 ± 0.09	0.13 ± 0.06	0.13 ± 0.19	0.04 ± 0.04	0.47 ± 0.68* (0.14 ± 0.17)	0.02 ± 0.03 (0.02 ± 0.01)	0.03 ± 0.03	0.03 ± 0.03	0.12 ± 0.07	0.15 ± 0.14

*MARGA results highly overestimated, because no concentration column was used.

5.3 Chemical composition of particles at different sites and seasons

We used the filter methods with the PM_1, $PM_{2.5}$ and PM_{10} cut-offs to measure the chemical composition of particles in Virolahti (**Paper II**) as well as in Helsinki and Hyytiälä (**Papers III and V**). The calculated average concentrations appear in Table 8.

Of all the inorganic ions measured, sulphate was the major contributor to the composition of PM_{10} and $PM_{2.5}$ at all the measurement sites. As expected, the sulphate concentrations were highest in Helsinki (3.5 μg m^{-3} in PM_{10} in the winter), most likely due to the contribution of fossil fuels burned for heating. The concentrations rose to the same level as those at the Virolahti background station during the first wildfire episode, but were lowest (0.7–1.3 μg m^{-3}) in Hyytiälä. Interestingly, the background sulphate concentrations were at the same level or lower in winter than in summer, most likely due to the faster oxidation of SO_2 to SO_4^{2-} in light and warm summer conditions.

Because of the contribution of the traffic emissions, nitrate concentrations were markedly higher in Helsinki (2.1 μg m^{-3} in PM_{10} in the winter), higher even than Virolahti concentrations during the wildfire episodes (1.1 and 0.5 μg m^{-3}). The background concentrations at Virolahti were on the same level as those in Hyytiälä: around 0.3 μg m^{-3} in summer and 0.5 μg m^{-3} in winter. Chloride originates mainly from sea salt, so concentrations were elevated at the sites close to the coast in Helsinki and Virolahti during the spring or winter periods (0.2 μg m^{-3}), when stormy winds occasionally blow in from the sea.

At the rural background sites, the concentration of ammonium was higher in summer (about 0.6 μg m^{-3}) and lower during the other seasons (0.3-0.4 μg m^{-3}). In Helsinki, the mean concentrations were 1.2 and 0.8 μg m^{-3} in winter and spring, respectively.

At all the sites, the magnesium concentration remained low, yielding average concentrations of 0.02–0.03 μg m^{-3}. However, during the New Year celebrations in Helsinki (which involved fireworks), magnesium concentrations increased dramatically. Calcium is a compound that originates in the soil, so Ca concentrations at background sites were low (0.03–0.04 μg m^{-3}) during the winter periods, when the ground was covered with snow. In summer, however, the concentrations (0.14 μg m^{-3}) rose to the same level as in Helsinki during the snowy and icy period of winter, when grit was spread on roads. The mean potassium concentrations were roughly 0.05 μg m^{-3}, except during the fire episodes in Virolahti (~0.2 μg m^{-3}) and in Helsinki during the winter period (0.14 μg m^{-3}), likely because of the elevated wood burning used for heating homes in winter

in the residential area of Kumpula, which has a predominance of detached houses. In Hyytiälä, the potassium concentrations increased rapidly on Midsummer night due to traditional bonfires.

5.3.1 Wildfire episodes

The mass concentrations of particles rose dramatically in Virolahti during two wildfire episodes in 2006 (**Paper II**). PM_{10} values even beyond the EU limit values were measured on three fire days (3 and 5 May, and 13 August), when the average daily PM_{10} values peaked at 55, 53 and 55 μg m^{-3} and the PM_1 mass peaked at 33 μg m^{-3} (on 5 May). During the fire days, the mass of the smallest particles ($PM_{2.5}$ and PM_1) in particular increased. Moreover, the chemical composition of the particles on the fire days differed from that of the particles on background days. In both the submicron and 1- to 2.5-μm size ranges, the mean of potassium, one of the biomass burning tracers, was about four-fold higher than on summer background days, but for the coarse particles was only about twice as high. During the episodes, the concentration of ammonium in submicron particles as well as that of nitrate in particles smaller than 2.5 μm rose. The mean concentration of sulphate in Virolahti during the first fire episode was on the same level as that measured in Helsinki in winter. However, the concentrations of sodium in Virolahti fell, and the other two typical sea salt compounds (Mg^{2+} and Cl^-) remained as low as on the summer background days.

6 REVIEW OF ARTICLES AND AUTHOR'S CONTRIBUTIONS

Paper I: In this study, we compared different measurement methods for sulphur dioxide and particulate sulphate at Virolahti: a monitor, two- and three-stage filter packs, an absorption solution (which had previously served in monitoring at national network stations), and a passive sampler. My personal contribution to this study involved setting up the sampling instrument, preparing the diffusive samplers, performing the analysis, and verifying the data with the help of the FMI technical staff. I also analyzed the data and wrote the article with the help of the co-author.

Paper II presents a study of the chemical composition of $PM_{1.0}$, $PM_{2.5}$ and PM_{10} particles during different seasons and during wildfires in 2006. I was responsible for the sampling, IC and ICP-MS analysis, data handling and writing of the article.

Paper III was the first study involving the MARGA 2S instrument. Measurements of major inorganic ions and water-soluble gases were carried out at the SMEAR III station in Helsinki in 2009–2010. We validated the method and studied the suitability of the instrument in Nordic winter conditions. I was responsible for running the instrument, analyzing and handling the data, and writing the article.

Paper IV concerns changes in the concentration of reduced nitrogen (NH_3+NH_4)–N in the air in Finland between 1990 and 2007. I was responsible for the chemical analysis and contributed to writing the article.

Paper V is based on the MARGA 2S measurements at the SMEARII station in Hyytiälä in 2010–2011. I was responsible for running the MARGA instrument and filter comparisons, analyzing and handling the data, and writing the article.

7 CONCLUSIONS

The aim of this thesis was to study the variability of inorganic gases and particulate matter in ambient air, to determine whether the novel online techniques presented here would prove suitable for background air quality measurements, and to study the comparability of data collected earlier with different sampling methods, which is important for studying trends.

In the study of the size distribution and chemical composition of PM_{10}, $PM_{2.5}$ and PM_1, about 70–80% of the toxic trace elements (lead, cadmium, arsenic and nickel) and PAH compounds were present in submicron particles. In practice, all the PAHs found were in particles smaller than 2.5 μm. For PAHs and trace elements, it would be more beneficial to analyze $PM_{2.5}$ or even $PM_{1.0}$ instead of PM_{10} in order to minimize the matrix effects during the analysis.

We studied the trends of reduced nitrogen and found that they decreased in southern and central Finland between 1990–2013. The concentrations in Finland are strongly influenced not only by changes in European emissions patterns, but also by changes in the transport pathways of air masses.

In this thesis, online ion chromatography proved successful with a one-hour time resolution for measuring ammonia, acidic gases (SO_2, HONO and HNO_3), and the chemical composition of particles at low background concentrations. This short-time resolution data served to configure the seasonal and diurnal cycles of inorganic gases. It also enabled us to detect short-term episodes.

In future atmospheric studies will use an online ion chromatograph connected to a mass spectrometer in order to identify new compounds.

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